

ORGANIC MATTER IN RIA SEDIMENTS: RELEVANCE OF TERRESTIAL SOURCES AND TEMPORAL VARIATIONS IN RATES OF ACCUMULATION

Graham Evans¹, Ricardo Prego^{2*} and John E. Marshall¹

¹ School of Oceanography and Earth Sciences, University of Southampton, National Oceanography Centre, European Way, Southampton SO4 3ZH, UK.

² Marine Research Institute (CSIC). Eduardo Cabello, 6; E-36208 Vigo, Spain.

* Corresponding author: prego@iim.csic.es

Abstract. The Ria of Vigo, one of the classical rias of SW Europe, is an environment of high production of organic matter naturally induced by the Galician upwelling. The organic matter is partly supplied by small rivers but mainly by sewage plants along the ria shoreline; jointly they contribute $725 \text{ t} \cdot \text{y}^{-1}$ of POC, of which 72% is of anthropogenic origin. The freshwater flux is equivalent to a supply of $5 \text{ g} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ of allochthonous POC to the ria floor. However the rate of accumulation of POC is dominated by the tenfold higher supply of autochthonous material from the net primary production. The present accumulation rate of organic matter ($49\text{-}58 \text{ g}_{\text{POC}} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$) is lower than the average supply, estimated from the sedimentary record, to the ria since the middle of the nineteenth Century ($>60 \text{ g}_{\text{POC}} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$). This difference may be due to anthropogenic activity or changes in the upwelling pattern. The composition of the organic matter in the sediment reflects the relative importance of the various sources (terrestrial-marine). While terrestrial woody materials dominate the inner ria, phytoplankton remains dominate the remainder of the ria. Rock-Evaluation analysis indicates the inner ria is the site of deposition of gas-prone material and it is inferred that the outer ria of oil-prone organic matter. The controls on the accumulation of POC in the rias show many differences to those found in estuaries affected by anthropogenic activities e.g. agriculture and increasing human population.

Key words: POM, POC, flux, autochthonous, allochthonous, rock evaluation analyses, NW Spain.

1 INTRODUCTION AND OBJECTIVES

2 The shelf zones in general, and particularly the coastal systems, behave as carbon traps
3 (Romankevich, 1984; Wollast, 1991) where part of the organic matter in the overlying waters
4 accumulates in the underlying sediments. In pristine systems, the source of that matter may be
5 dominated by autochthonous material from net primary production (NPP), and allochthonous
6 material supplied by rivers, or both together. Natural eutrophication may sometimes occur due
7 to nutrient loadings and from discharges of industrial plants and sewage treatment works and
8 from other human-influenced 'diffuse sources' such as run-off from agricultural catchments that
9 may increase the water eutrophication effects (de Jonge et al., 2002). The enrichment of water
10 by nutrients causes an accelerated growth of algae to provide the causes of eutrophication (de
11 Jonge and Elliott, 2002).

12 An important fate for both NPP and terrestrial organic matter is burial in the coastal
13 sediments. Thus, it is important to understand the trophic conditions of the coastal system and
14 the sedimentation rate of organic matter. In coastal systems in areas of upwelling, such as the
15 Galician Rias, the impact of allochthonous contributions of organic matter may be different to
16 that of oligotrophic environments where eutrophication may increase productivity as in some
17 shallow seas and coastal lagoons, e.g. the North Sea (Peeters et al., 1993) and the Wadden Sea
18 (de Jonge et al., 1996) sea.

19 Typical estuarine systems have been extensively investigated. Eutrophication is related to
20 agriculture activities and the increasing human population which has occurred in several of the
21 world estuaries (de Jonge et al., 2002). The ria is another type of coastal system which although
22 classically developed in the Iberian Peninsula, also occurs elsewhere in Brittany in France and

1 Devon and Cornwall in the British Isles, Korea, parts of the Chinese and the Argentina coasts. Ria
2 is a useful term capable of wide application that should not be locally restricted (Evans and
3 Prego, 2003). The budget of autochthonous and allochthonous organic matter and its fate in the
4 sediments of rias has been poorly studied and is still not completely understood.

5 The rias of the Galician coast, NW Spain, have attracted considerable attention from
6 scientists since Von Richtofen (1886) introduced the term 'ria' into the geological literature,
7 using Galicia as the type area for this feature. Later, the geomorphological evolution of the area
8 has been studied by workers of various nationalities (see review by Sala, 1984) and the
9 sediments were first comprehensively studied by Dutch workers under the leadership of
10 Pannekoek (Pannekoek, 1966; 1970). Subsequently, contributions were made by the geologists
11 of the 'Instituto Español de Oceanografía' (viz. Rey, 1993), the 'Instituto de Investigaciones
12 Marinas (CSIC)' (Bernárdez et al., 2005; 2006 and the references cited therein), and the
13 University de Vigo (see review in Vilas et al., 2005; Mendez and Vilas, 2005; Garcia et al., 2005).
14 Recently, a series of detailed maps were produced of the bottom sediments of the Vigo and
15 adjacent rias (Vilas et al., 2005). However, the main interest in the Galician Rias has been for
16 oceanographers, because of the fertility and the important commercial fisheries (Díez et al.,
17 2000). The relatively high content of organic matter of the bottom sediments has been noted
18 and discussed by several workers since the early pioneering studies of Margalef (1956),
19 Margalef and Andreu (1958) and Fraga (1960) although little information has been provided on
20 its nature and composition. The existing information was mainly provided by Diz et al. (2002)
21 and Alvarez et al. (2005) who studied the variation in a vertical core of various biomarkers and
22 showed the temporal variation of the types of organic matter which have been supplied to the

1 Ria of Vigo.

2 In order to attempt to provide a comprehensive understanding of the behaviour and fate
3 of organic matter in ria systems this study evaluates the importance of the allochthonous
4 contributions of organic carbon and provides an estimate of the relevance of various sources as
5 well as the temporal rate of accumulation of particulate organic matter in the sediment.

7 ***Survey area: The Ria of Vigo***

8 The main Ria of Vigo has an area of 156 km², is approximately 31 km long and gradually
9 narrows landwards from 6 km near its mouth to 0.6 km near the narrow Rande Strait; beyond
10 which it widens into a wide shallow bay with an area of 18 km²: the San Simón Bay (Fig.1).
11 Depths vary from 60 m near the entrance of Ria of Vigo to the inner part the San Simón Bay
12 landward of this narrows is less than 5 m over most of its subaqueous part. At the landward
13 head of the ría are broad intertidal sand and mud-flats cut by estuarine channels which form
14 part of a bayhead delta; interestingly, except in a small area partly protected by sea walls,
15 marshes dominated by halophytic plants are absent, although much of the mudflat is colonized
16 by *Zostera sp.*

17 Several small to medium sized rivers drain an area of 489 km² before discharging in to the
18 Ria of Vigo. The main discharge is carried into the landward part of the San Simón Bay by the
19 river Oitavén and the small streams of Ullo, Sidral, Maior and Alvedosa. A few smaller streams
20 such as the Lagares, Postrillón and Fraga enter the middle-outer ría. The Oitavén River is the
21 main tributary contributing around 80% of the total freshwater input to the ria, whose annual
22 average flow is 17 m³·s⁻¹, ranging from 55 m³·s⁻¹ in February to 1 m³·s⁻¹ in August (Río-Barja and

Rodríguez-Léstregas, 1992). Early work by Nombela (1989) showed that in the San Simón Bay, the Alvedosa River ($\approx 2 \text{ m}^3 \cdot \text{s}^{-1}$), although one of the smallest streams has discharges and loads greater than the other streams. Similarly, the Lagares River ($\approx 4 \text{ m}^3 \cdot \text{s}^{-1}$), also a relatively small stream, has the highest discharge and sediment load of all the rivers in the outer ria.

The catchment area of the rivers is dominated by hard PreCambrian and Palaeozoic granites, gneisses, mica-schists and some quartzites. The region surrounding the ria has a warm humid climate. Much of the hinterland is covered by forest and scrub with pasturelands composed of heath with grasses being common (Valdés and Gil-Sánchez, 2001); cultivated land occupies only a small part of the rivers catchments, e.g 12.5% of the Oitavén, and 42.5% in the catchment of the Alvedosa River which is the exception (Pazos et al., 2000). Frequent forest fires occur and these strip the landscape of vegetation. However, the land soon recovers, usually after 1-2 years (Díaz Fierros et al., 1987). Benito et al. (1991) claimed that most of the erosion occurs during the first six months of rain after the fires.

The Ria of Vigo is mesotidal (average tidal range 2.2 m). Its outer and middle zone is mainly oceanic with water salinities >35 decreasing to 31-32 in the Rande Strait and to even lower values <15 around the small river estuaries at the landward head of the San Simón Bay, which is the estuarine ria zone (Evans and Prego, 2003). Generally, the ria has a positive estuarine circulation with water flowing landward along the deeper parts and seawards at the surface separated by a narrow zone of mixing (Otto, 1975; Prego et al., 1990). Water residence times in the ria range from a few days to a month, usually due to fluvial forcing during the wet season and by upwelling events during the dry season (Prego and Fraga, 1992). The circulation of water and nutrients in the Ria of Vigo and adjacent rias as well as their productivity is greatly

1 influenced by the Finisterre marine upwelling which usually occurs from April to October
2 (Blanton et al., 1984) and forces Eastern North Atlantic Central Water (Fraga, 1981) into the
3 interior of the rias (Prego and Bao, 1997). Thus, the primary production in the ria is high and in
4 the middle zone of the Ria of Vigo ranges between 30 to 100 $\text{mgC}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ in winter, but this
5 increases to 700 to 1200 $\text{mgC}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ during the rest of the year (Vives and Fraga, 1961).

6 The importance of anthropogenic activities has increased historically; shipbuilding
7 becomes important at the end of the 19C. However, the biggest increases have been since the
8 1960s (Howarth et al., 2005), including mussel aquaculture, since when there has been a
9 marked increase in population and industrial activity (Fig.2).

11 **MATERIAL AND METHODS**

12 ***Water and sediment sampling***

13 The Oitavén River discharge was measured daily at the Sotomaior gauging station. It was
14 calibrated in 2004 by in situ measurements with current-meters as the method 'area-speed'
15 (WMO, 1994) and the river flow corrected to its entire basin surface according to the rainfall
16 and land used by a hydrological model (Alvarez-Eijo, 2000). The smaller stream flows were
17 calculated from the Oitavén discharge and the stream basin areas due to the good relationships
18 ($r^2 > 0.9$) obtained by comparing the measurements of their flows (Alvarez-Eijo, 2000). Sewage
19 treatment plants (STPs) flows corresponding to the monthly average discharge during 2004
20 were provided by the Sewage Plant Companies.

21 Samples from the rivers and STPs were collected and placed in 1-L glass bottles. Fluvial
22 sampling points (salinity < 0.1 measured with a WTW MultiLine P4) were situated on the Oitavén

1 River, streams of Alvedosa, Lagares, Fraga, Maior and Ullo and the STPs at Vigo, Teis, Arcade,
2 Redondela, Cangas and Moaña (Fig.1). Each point was sampled monthly during 2004, except for
3 the Oitavén River which was sampled twice a month.

4 Sediment samples were collected from the ria floor using a standard Van-Veen stainless
5 steel grab and a box corer (see Fig.1 for locations). Cores were taken to sample the undisturbed
6 sediment from the box-corers and samples were collected at 1 cm intervals.

8 ***Sample pre-treatment and analysis***

9 Freshwater and sewage samples were refrigerated at 4°C and taken to the laboratory on
10 the same day; and, were vacuum filtered, 1 L for the rivers and the small streams and 200 mL
11 for EDARs, through weighed Whatman GF/F filters (0.45 µm filter circles of 2.5 cm diameter) in
12 a filter holder (Pall, Gelman). This was used to operationally define the separation between
13 dissolved and particulate components (Chapman, 1992; Loring and Rantala, 1992). Wet filters
14 containing the suspended particulate matter (SPM) were put into a laminar flow chamber until
15 dry. The filters were then weighed to calculate the SPM concentration, placed in Petri dishes
16 and stored at –20°C in the freezer until POC analyses. Funnels, bottles, filter holders, tweezers,
17 Petri dishes and other materials were washed with detergent and rinsed with Milli-Q water.

18 Particulate organic carbon (POC) in the suspended particulate matter was determined
19 combustiometrically analyzing the filters in the EA 1108 CNH analyzer (Carlo Erba Instruments)
20 of the Analytical Service (SAI) of Coruña University (UDC). The analysis of blank filters showed
21 negligible amounts of carbon and acetanilide was used as standard. The concentration of POC
22 (mass/volume) in each sample was calculated multiplying the POC (mass/mass) by SPM

(mass/volume) concentration. Finally, the flux of POC was calculated for each source - river, small streams and EDARs - multiplying each water flow by its POC concentration (mass/volume).

Standard grain size techniques were used to determine the sand, silt and clay content of the samples (Folk 1974). Carbonates were previously removed by acidifying the sediment subsamples and the organic carbon was later determined using a standard Perkin-Elmer elemental analyzer apparatus.

Other samples were used for the study of the composition of the organic matter. They were first dried and the large shell fragments removed which otherwise would distort the analyses. They were then weighed and initially treated with concentrated commercial grade HCl to remove carbonates and mobilise any calcium that otherwise interfere with the removal of silicates. This acid treatment was followed by washing until neutral. The silicate removal was achieved with 60% HF acid, initially at low concentration by adding to the sample already in water. After any initial reaction had subsided the acid strength was increased by decanting off the spent acid and recharging with fresh acid. The samples were again decanted and washed until neutral and concentrated HCl added. They were brought to boiling and then rapidly diluted with a large volume of water followed by further sieving at 20 μm . This final acid treatment removed any neoformed fluorides. The resulting kerogen concentrate was checked for quality and then stored in a vial. Samples rich in amorphous organic matter (AOM) were split with one half having the AOM removed using a tunable ultrasonic probe. This preferentially fragments the AOM particles that can then be removed by sieving at 20 μm . Finally, a small part of the kerogen concentrate was mounted on a glass coverslip with Elvacite 2044.

The sediment samples were then examined microscopically and the abundance of the

different components determined by point counting as particles to a total count of 400. A relatively simple classification was used into some nine general categories. AOM was not included in the count. The results have been recalculated to remove the effects of data closure inherent in all proportional data the results were also converted to an eight point logarithmic abundance class scale following Kovach and Batten (1994).

The samples used for the Rock-Eval analysis were taken from the top of the box cores and placed in a cold box before being deep frozen and transported immediately to France. They were analyzed by Étienne Brosse of the geochemical laboratories of the 'Institut Français du Pétrole' using standard RockEval procedures (e.g. Tissot and Welte, 1984).

RESULTS

Continental POC contributions to the ria

The annual ranges of POC concentration introduced by the six STPs situated in the littoral of the Ria of Vigo are shown in the Table 1. The annual average varied in the small treatment plants from 1.6 to 3.7 mgPOC·L⁻¹ in four of the treatment plants; but there was an increase to 29.1 mgPOC·L⁻¹ in the Teis STP where the treatment seems to have been poor. The most important plant, Vigo STP, where sewage from 300,000 inhabitants is processed, has a POC content (5.1 mgPOC·L⁻¹) of the same order as that of the small plants. The impact of these wastewaters into the Ria environment also depends on the discharge, which is lower than 0.1 m³·s⁻¹ for Arcade, Redondela, Cangas and Moaña STP; therefore, their annual loads are very low (fifty times lower) in comparison with that from Vigo STP (9.7 gPOC·s⁻¹), to the latter's significant flow (1.95 m³·s⁻¹). On the other hand, the load from the Teis STP, is due to its higher

1 concentration of POC since its flow is low ($0.07 \text{ m}^3 \cdot \text{s}^{-1}$), a not insignificant: $2.0 \text{ gPOC} \cdot \text{s}^{-1}$.

2 While the STP loads were calculated on the basis of monthly data, the river POC
3 contributions could be calculated daily from the flows because there is a significant relationship
4 between the flow and the POC flux, as it is indicated by the equations of Table 2, from a similar
5 calculation procedure that to iron in the Ria of Vigo (Filgueiras and Prego, 2007). Except for the
6 Maior and Ullo streams, the annual load variation is low, ranging from $0.9 \text{ gPOC} \cdot \text{s}^{-1}$ (Fraga
7 stream) to $3.5 \text{ gPOC} \cdot \text{s}^{-1}$ (Oitavén River), Table 2.

8 As a whole, the Ria of Vigo receives annually $721 \text{ t} \cdot \text{yr}^{-1}$ ($20 \text{ g} \cdot \text{s}^{-1}$) of allochthonous POC,
9 according to the fluxes shown in Fig.3. There are two main sources of allochthonous POC. One is
10 natural (one third of total) and is introduced by the rivers that are dominated by the
11 contribution of unpolluted River Oitavén, which carries 16% of the allochthonous POC inputs. The
12 other is anthropogenic (two thirds of total) from the treatment plants, of which 55% of the
13 allochthonous POC to the ria is supplied by the Vigo STP.

15 ***Organic matter in ria sediments***

16 The organic matter of the bottom sediments varies from high values in the axial parts of
17 the main ria and the outer parts of the San Simón Bay with lower values along the flanks and in
18 the inner parts of the Bay. The organic carbon shows little or no consistent pattern with depth
19 in the topmost 30 cm of sediment studied in the box cores from the San Simón Bay. The values
20 are within the same range as the surface samples (i.e. 2.0-5.0%) except for a few isolated values
21 of 6.0-7.0% (Fig.4a). On the other hand, the nitrogen content of the surface sediments of the
22 San Simón Bay are rather variable and are usually are between 0.4-0.5 percent (Fig.4b). As with

1 the organic carbon, the same range of values occur at depth, at least as far down as 30 cm
2 without any discernable variation. Carbon- nitrogen ratios vary from 3.0-13.3 with the highest
3 values occurring near the Rande Strait.

4 Examination of the organic fraction of selected samples of the bottom sediments of the
5 Ria (see Fig.1 for locations) show that there are marked differences between those of the outer
6 Ria and those of the San Simón Bay (Table 3). This is in the form of the abundance of terrestrial
7 phytoclast, both light wood, plant tissue and the much less abundant dark wood. The latter is
8 effectively confined to the Bay. Plant tissue declines steeply away from the margins of the Bay
9 and the source of terrestrial input. Other components, which show marked changes, are
10 dinoflagellate cysts that progressively increase away from the sources of terrestrial input and
11 conversely the cuticles that show an inverse decline within the Bay.

12 Significantly, the presence of the thickets of *Zostera sp.* in the northern part of the Bay
13 (samples 1 and 8; Fig.1) appear to have no effect on the proportions of cuticle and tissue and
14 are presumably not contributing to the mineral acid resistant palynological residue. As regards
15 the outer part of the Ria system there is evidence for an increasing marine influence within the
16 palynofacies. Primarily, this takes the form of an abundance of dinoflagellate cysts. The outer
17 Ria also shows the concentration of more mobile palynomorphs primarily bisaccate pollen
18 which reach a maxima before declining seawards. An interesting group is the foraminiferal test
19 linings which show a progressive increase throughout the system. In estuaries, the work of Farr
20 (1989) has shown that they are generally well mixed systems with little segregation of marine
21 and terrestrial components. Here, it appears that the test linings, which normally originate from
22 benthic foraminifera that live within the sediment, have the potential to provide an *in situ*

1 signal. The presence of AOM (Amorphous Organic Matter) only in the outer Ria indicates that
2 there the effect of increased productivity/enhanced preservation has been to preserve part of
3 the otherwise unfossilised component of the phytoplankton. The logarithmic abundance class
4 scale also shows these trends. This transformation removes the closure from the data and
5 provides a method for revealing broad trends within the system. This emphasises the restriction
6 of the light and dark wood phytoclast groups to the Bay together with a minor peak in spores.
7 The increase in dinoflagellate cysts from the Bay to outer the Ria is also shown (Fig.5). Again,
8 this transformed data shows the marked progressive increase in foraminiferal test linings
9 seaward.

10 These variations in the various components are shown clearly by the logarithmic class
11 scale. Such a transformation removes the closure from the data and reveals the broad trends. It
12 emphasises the restriction of the light and dark wood phytoclasts to the San Simón Bay and also
13 the minor peak of spores. The increase in dinoflagellate cysts as well as the progressive increase
14 in foraminiferal test linings from the San Simón Bay, towards the seaward mouth of the rias is
15 clearly shown.

16 The Rock-Eval evaluation parameters show that the sediments are characterized by
17 immature organic matter as would be expected in recently deposited sediments (Table 4). The
18 S_2 values indicate that they have a relatively good potential as a source of hydrocarbons. The HI
19 (Hydrogen Index, S_2 normalised by TOC) suggests that the organic matter appears to be of
20 kerogen type III and is dominantly of continental rather than marine origin.

DISCUSSION

Quantitative significance of Allochthonous POC contributions

The Ria of Vigo, in common with other Galician rias, receives particulate organic matter from several sources. The allochthonous supply is dominated by material carried into the rias by the rivers from the heavily vegetated hinterland. Also, an important source, which has increased in importance since the growth of the local population and industries, is the sewage and industrial waste from the urban centres which surround the Ria (Evans et al., 2000). The inputs from fluvial and sewage sources is currently estimated to be $725 \text{ t}\cdot\text{y}^{-1}$ of POC of which 67% is derived from treatment plants and 5% from the polluted Lagares River. Until now, the continental inputs of POC to the Ria of Vigo were evaluated as being due to a supply by the pristine Oitavén River (Gago et al., 2005). These authors calculated its contribution to be $97 \text{ t}\cdot\text{y}^{-1}$. In the present study the POC flux from the Oitavén has been calculated to have a similar value, i.e. $112 \text{ t}\cdot\text{y}^{-1}$. However, other freshwater inputs to the ria must also be taken into account (Fig.3). When the loads of all the inflowing streams are considered, the fluvial discharges of POC is estimated to be $241 \text{ t}\cdot\text{y}^{-1}$ and in addition, there is $484 \text{ t}\cdot\text{y}^{-1}$ of POC from the sewage treatment plants. Consequently, the total continental contribution of POC to the ria is approximately 7.5 times higher than previous evaluations and 72% of this total POC is of anthropogenic origin. Interestingly, as a whole, the POC flux corresponds to an average concentration of $0.78 \text{ mg}\cdot\text{L}^{-1}$ of POC, which is lower than the average for unpolluted rivers proposed by Meybeck (1982).

The importance of these allochthonous contributions of POC to the ria as an organic reservoir can be only defined when their autochthonous POC fluxes are known. The latter are a result of the processes of photosynthesis, remineralization, and sedimentation inside the Ria of

Vigo and were quantified using a reservoir budget (Prego 1993a,b) summarized in Figure 6. The Ria of Vigo is, as are the other Galician Rias, the site of deposition of sediments relatively rich in organic matter. It is an area of high productivity due to eutrophic events of upwelling and extensive photosynthesis in the photic layer of the water column. It has been estimated the mean photosynthesis rate in the Ria of Vigo is $350 \text{ mgC}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. This is in agreement with those measured previously by Vives and Fraga (1961) and Fraga (1976) in the Ria of Vigo and Varela et al. (2005) in other rias.

Because the rias are zones of relative high primary production compared with nearby oceanic regions (Finenko, 1978), they exhibit elevated processes of remineralisation and sedimentation of the organic matter. Consequently, although some of the POC supplied to the ria is lost to the open sea (19%) due to the estuarine circulation and some to mineralization (41%) a considerable amount is trapped in the bottom sediments (34% or 41% if the mussel removal is included; i.e. $144 \text{ mgC}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$). The Ria behaves like a carbon trap and presents similar average rate of POC on the continental margin suggested by Romankevich, (1984) during the Late Quaternary or in coastal zones estimated by Wollast (1991). The composition of the POC accumulating in the sediment reflects the importance of the various sources. Today, the contemporary supply of POC to the floor of the ria is dominated by autochthonous material ($44\text{--}53 \text{ g}_{\text{POC}}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) whilst allochthonous material contributes ($5 \text{ g}_{\text{POC}}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$). These rates are based on one year measurements and of course they may vary; however, at the moment, the extent of this variation is unknown although the year of measurement may be considered meteorologically as a standard year.

The POC fluxes show that the natural eutrophication during the upwelling events (Prego et

al., 1999; Prego, 2002) controls the POC budget in the ria. Moreover, when the causes (nutrients) and the results (POC increase) of eutrophication are considered (de Jonge and Elliott, 2002) in rias the allochthonous POC, which is mainly anthropogenic, cannot increase the water eutrophication effects because the allochthonous sources of POC are very low in comparison with the autochthonous. When the pattern of flux of POC to rias is compared with that of the typical world estuaries affected by agriculture and increasing human population, e.g. the Humber (Boyes and Elliott, 2006), they are different in many ways (de Jonge et al., 2002).

Deposition and nature of POM in the bottom sediments

The bottom sediments of the San Simón Bay contain similar carbon contents with the greatest values (>5.0%) in the fine grained sediments which extend into the Bay from the Rande Strait (Nombela et al 1995; Belunze-Segarra et al 1997). Analysis of the inner ria sediments by rock-evaluation techniques has confirmed that the POC accumulation in the inner parts of the San Simón Bay is of dominantly terrestrial sources and has a good hydrocarbon potential. There is considerable gas produced in the ria sediments. This was first reported by Acosta (1981) in the sediments of Muros Ria. Later studies of the sediments of San Simón by Nombela et al (1995) and later by Alvarez-Iglesias (2006) showed an abundance of small gas cavities in the sediments of the outer part of the bay around the mussel rafts (Nombela et al., 1995). Detailed geophysical studies by Rey (1993) and subsequent work by Garcia Gil et al. (1999) have revealed what appears to be abundant evidence of gas in the contemporary sediments of the Ria of Vigo. Unfortunately, no rock-evaluation studies were able to be made of the outer ria sediments. However, from the palynological analysis, it would seem likely that these sediments would be

1 richer in type I kerogen and more oil-prone than the gas-prone sediments of San Simón Bay. The
2 geometry of the sediment-fill of the Ria of Vigo and its grain size composition would make it a
3 potential future stratigraphic hydrocarbon trap i.e. an elongate mud-dominated organic rich
4 sediment body infilling an incised valley, which is what a ria really is (Evans and Prego, 2003).
5 This mud body passes landwards up-dip into a substantial sand body composed of clean washed
6 porous medium-fine sands of the ria-head delta which is capped by a sheet of intertidal and
7 marsh mud.

8 Consequently, the autochthonous-allochthonous organic material is not homogeneously
9 distributed in the ria sediments. Although the allochthonous contributions to the ria are small,
10 its inner part, i.e. San Simón Bay, is an estuarine domain where the continental influence is
11 important, as indicated by the sediment record. This part of the ria is more prone to change (see
12 Evans and Prego, 2003) and as shown by Varela et al. (2008) in the neighbouring Ria of
13 Pontevedra. This pattern is different from that observed in eutrophic estuaries, e.g. the Humber
14 (Boyes and Elliott, 2006).

15
16 There is some data on the rate of sedimentation in the Ria of Vigo. However, this proved
17 to be difficult in San Simón Bay due to the disturbance of bottom sediment by biological
18 reworking, waves and probable anthropogenic activity, possibly due to the dragging of nets,
19 became clear in the earlier studies by the University of Vigo and Imperial College (Evans et al.,
20 1994; Nombela et al. 1995). Attempts to obtain ^{14}C dates from good shell material taken from
21 some cores by Vilas, Evans and Nombela in the early 1990s, gave disparate results with no clear
22 relationship between age and depth beneath the sediment surface. Similarly, Howarth et al.

(2005) failed to obtain any unambiguous rates of sedimentation in the sub-aqueous parts of the San Simón Bay using ^{210}Pb dating. Nevertheless, the latter were able to determine the rate of sedimentation on a few small marshes on the landward parts of the San Simón Bay to be $5.6 \text{ mm}\cdot\text{yr}^{-1}$ based on ^{210}Pb , with the accumulation rate of sediment of $0.3 \text{ g}\cdot\text{cm}^{-1}\cdot\text{yr}^{-1}$ (confirmed by Cs dating which gave a rate of sedimentation of $5.0 \text{ mm}\cdot\text{yr}^{-1}$). Also Quintana et al. (2006) measured a rate of sedimentation of the uppermost sediment of the intertidal flats of the San Simón Bay of $5.6 \text{ mm}\cdot\text{yr}^{-1}$. Later Alvarez-Iglesias et al (2007) using ^{137}Cs and ^{210}Pb dating measured a rate of sedimentation of $3\text{-}6 \text{ mm}\cdot\text{yr}^{-1}$ on the intertidal flats of San Simón Bay. Also Pérez-Alvarez (2007), in a further study, determined a rate of sedimentation of $5\text{-}6 \text{ mm}\cdot\text{yr}^{-1}$ on the upper parts of the intertidal flats near the mouth of the Oitavén River. Alvarez-Iglesias et al. (2006) suggested that the rate of sedimentation in the sub-aqueous part of San Simón Bay would be slightly lower than this figure i.e. approximately $3.8 \text{ mm}\cdot\text{yr}^{-1}$.

Furthermore, preliminary examination of the pollen in a core, collected in 1988 by Evans, Vilas and Nombela from the middle of the San Simón Bay just west of Isla de San Simón, by Ms Ge Yuy (personal communication to G. Evans) showed the first appearance of *Eucalyptus sp.* pollen at approx 50 cm indicating a rate of deposition of $3.7 \text{ mm}\cdot\text{yr}^{-1}$ since 1856, (this is the date suggested for the introduction of Eucalyptus species by Desprat et al. (2003)). Later, a very detailed palynological study of a core from the deeper water of the middle of the Ria of Vigo by Desprat et al. (2003) showed the first appearance of *Eucalyptus sp* pollen at a depth which indicates a similar rate of sedimentation of $3.9 \text{ mm}\cdot\text{yr}^{-1}$ since 1856.

The core studied by Ms Ge Yuy from the middle of the San Simón Bay had an average sediment density of 1.06; so, if a value of between 4-5 % of POC (see Nombela et al 1995) is

1 taken as typical of the muddy sediment of the Bay, this indicates a rate of accumulation of
2 organic carbon of $160\text{-}200\text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ in the inner part of the ria (17.4 km^2 of surface area) since
3 the middle of the 19th Century. On the other hand, in the core studied by Despart et al. (2003)
4 from the main Ria of Vigo, if it is assumed that the average sediment density is 1.06 (no values
5 were given by these authors) and the organic carbon content of the upper sediment is taken to
6 be between 3-4 % (Diz et al. 2002), the rate of accumulation of organic carbon since the middle
7 of the 19th Century has been approximately $120\text{-}160\text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ in the middle part of the ria (39.0
8 km^2 of surface area). Moreover, two cores from the outer ria boundaries (Caetano et al., 2009;
9 Martins et al., 2011) have provided some additional data on rates of sedimentation using ^{14}C
10 dating which are rate disparate of 0.76 and $0.04\text{ cm}\cdot\text{yr}^{-1}$. The average of these gives a rate of
11 sedimentation of $0.39\text{ cm}\cdot\text{yr}^{-1}$; using the aforementioned weight of dried sediment per cm^3 and
12 an average POC content of $3.4\pm 0.3\%$; this indicates a rate of accumulation of organic carbon of
13 $135\text{-}160\text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ in the outer part of the ria (99.8 km^2 of surface area). Area-averaging the
14 sediment rates from the three parts of the ria gives a rate of accumulation of POC of $130\text{-}165$
15 $\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, which is greater than the present rate of production. However, if the lowest value of
16 $0.04\text{ cm}\cdot\text{yr}^{-1}$ is considered using the same sediment density and POC content, the rate of
17 accumulation of POC is only $15\text{-}20\text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ in the outer part of the ria. Then, area averaging the
18 sediment rates for the three parts of the ria gives a rate of accumulation of POC of $60\text{-}75\text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$
19 which is close to that of the present rate of production of $50\text{-}60\text{ g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$.

20 The contemporary supply of POC to the ria bottom is dominated by the autochthonous
21 organic carbon, which is more than ten times higher than the allochthonous supply from rivers
22 and sewage loads. Although there is an important inflow of sewage, which has increased the

1 supply of allochthonous POC, 16% of which is from the Oitavén River and 72% of which is of
2 anthropogenic origin; on the other hand, there has been a marked reduction of the area
3 covered by woodland in the river catchments feeding the ria. Also, there has been a further
4 reduction in the supply of sediment and associated POC by the Oitavén River, the main
5 sediment supplier to the ria, due to the construction of a dam which was completed in 1977.

6 There is a disparity between the rate of POC deposition today ($49\text{--}58 \text{ g}_{\text{POC}}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$) and the
7 estimated average rate of accumulation since the middle of the 19th Century: $>60 \text{ g}_{\text{POC}}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$.
8 Considering the large increase in human activities in the area bordering the Ria of Vigo since the
9 beginning of the 20th Century and particularly since 1960s with its concomitant discharge of
10 human and industrial wastes, the apparent reduction in the rate of accumulation of POC in the
11 sediments is rather surprising.

12 There are only a few dates to determine the latter, but they all yield rates which are the
13 same order of magnitude. There are several factors which might explain the apparent reduction
14 in the rate of POC accumulating on the floor of the ria. The process of the photosynthesis and
15 also the degree of preservation of POC in sediments may have been affected by the marked
16 increase of metals and other toxic substances which have been increasingly discharged into the
17 Ria of Vigo with human waste and from industrial complexes around the ria as well as from air
18 borne material from a bridge and intensive road networks (Howarth et al., 2005). Also, the
19 reduction of discharge of the Oitavén River due to the dam construction would have reduced
20 the supply of POC to the ria. In addition, this reduction in flow may have weakened the
21 estuarine circulation and made the ria a less efficient trap. However, due to the importance of
22 autochthonous contribution to the sediment, the apparent reduction in POC accumulation is

1 unlike to have resulted only from anthropogenic induced changes, but could possibly have
2 occurred due to mainly environmental changes. Different scenarios for the production of
3 phytoplankton in the rias under various climate circumstances have been proposed by Varela et
4 al. (2008). They showed that if the NE wind regime in summer is reduced (i.e. favourable
5 conditions for upwelling are reduced) a decrease in the phytoplankton production and biomass
6 should occur; similarly, a decrease in production would also occur if the runoff becomes lower
7 during spring. The opposite occurs when the runoff intensifies during spring or the NE winds
8 increase during the summer (although strong upwelling events could prevent phytoplankton
9 accumulation inside ria due to the increase of the ria outflow). Hence it may be hypothesized
10 that upwelling fluctuations controlled by climate changes, as stated in the Varela et al. (2008)
11 paper, are a possible reason to the temporal differences observed in the sedimentation rates of
12 POC. Again, this is another difference between rias and eutrophic estuaries.

13
14
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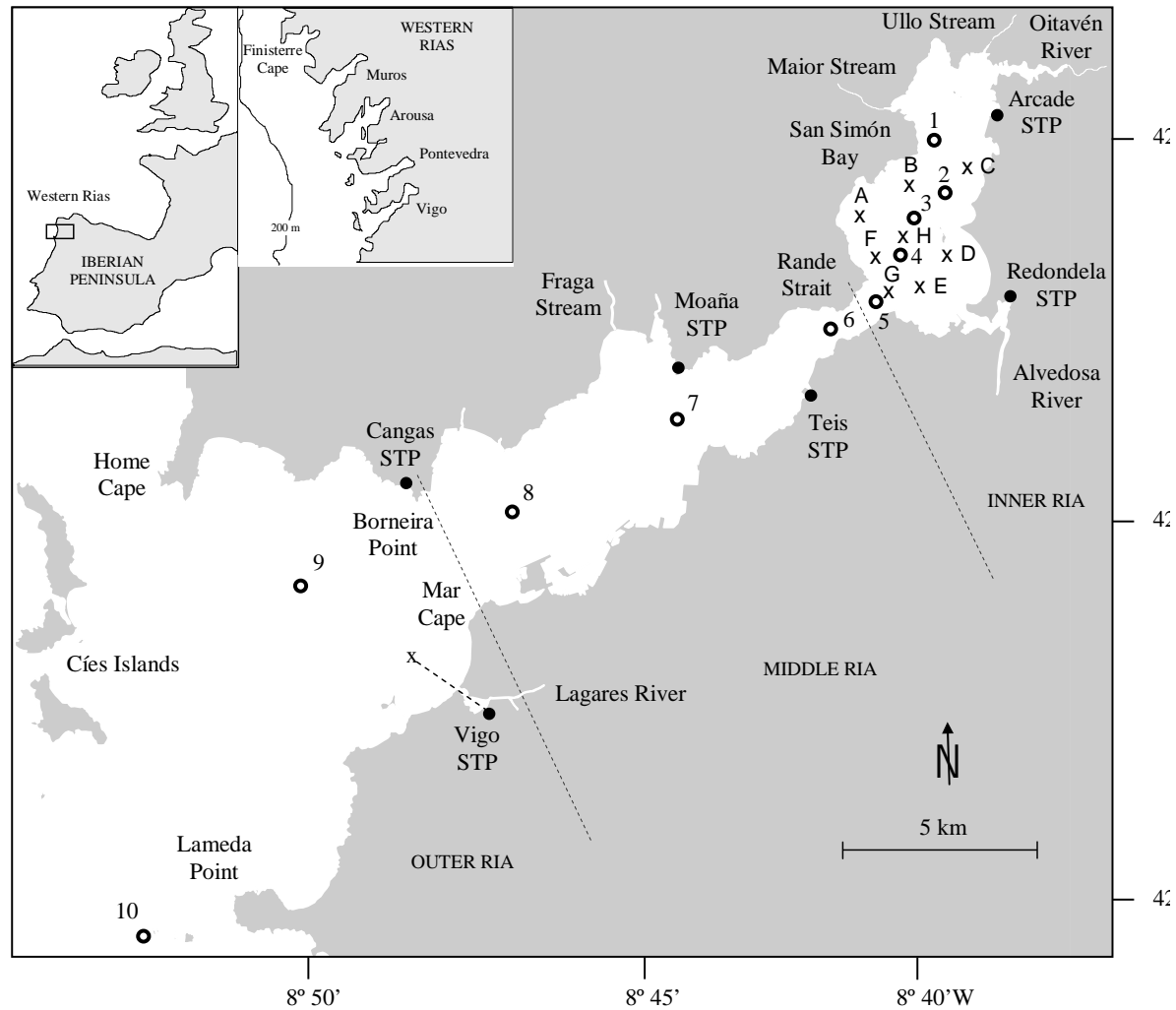
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 2 Figure 1. Ria of Vigo with their three main zones and geographical names. Rivers, sewage treatment plants (STP),
 3 submarine emissary of Vigo STP, surface sediment (st.1-10), box corer (st. A-H) used for carbon, nitrogen and rock-eval
 4 (st.B and D to H) are also shown.

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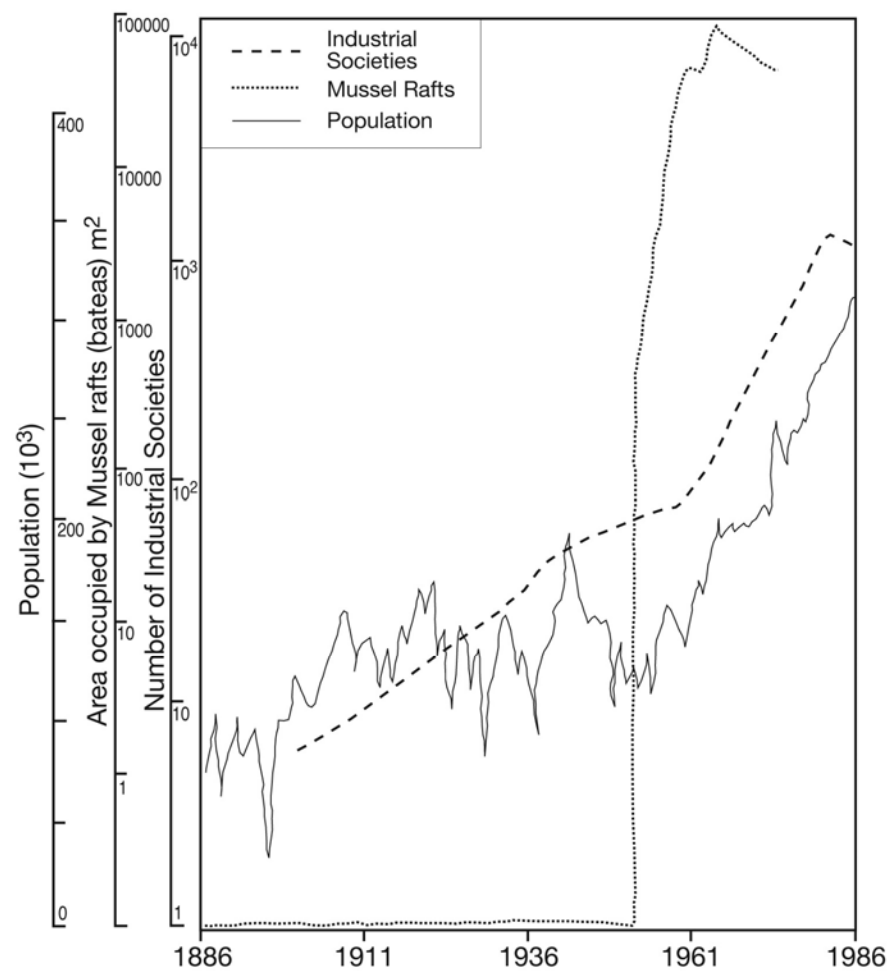


Figure 2. Human activity in the Vigo Ria area.

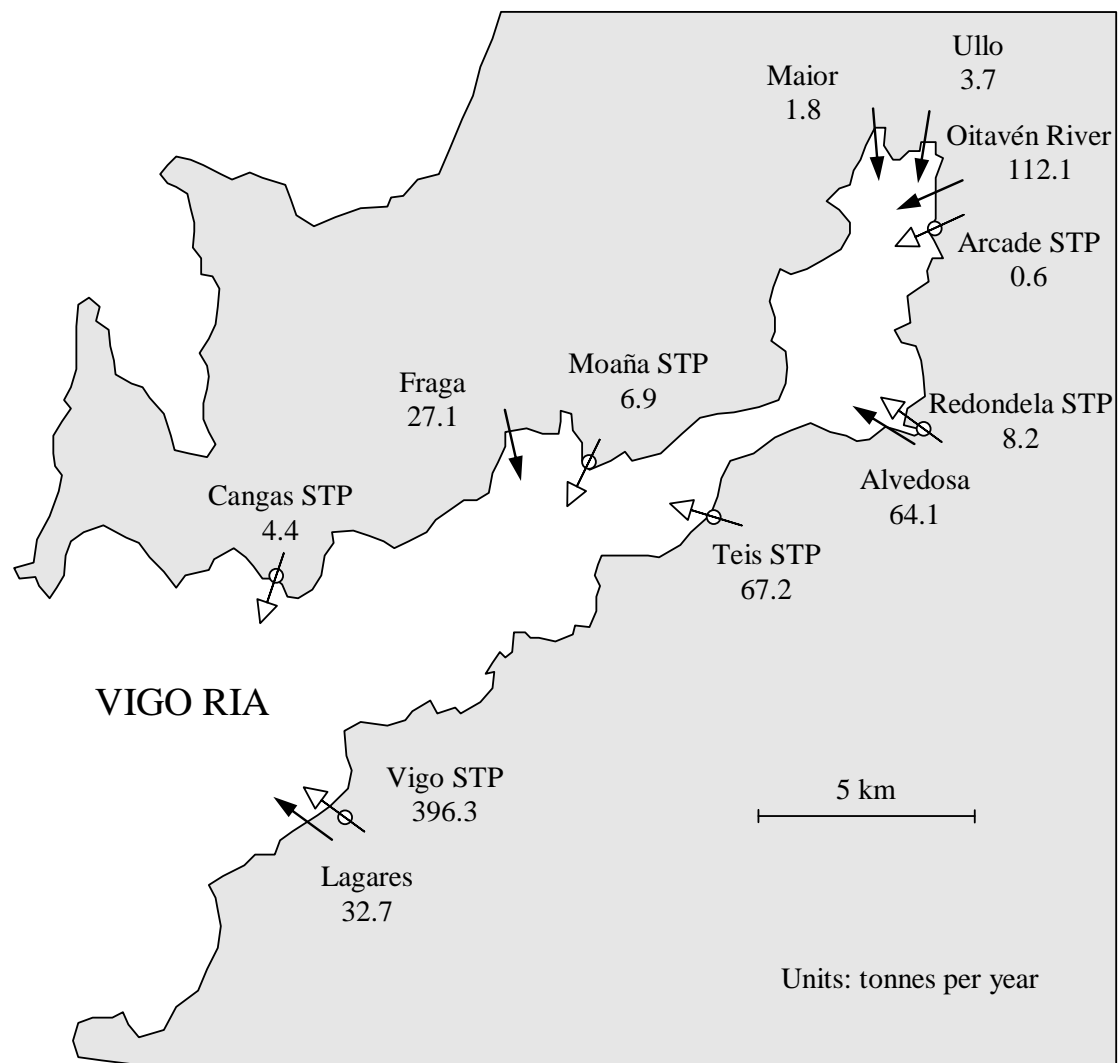


Figure 3. Allochthonous POC contributions to the Ría of Vigo. Black arrows correspond to river load and empty arrows to sewage discharges.

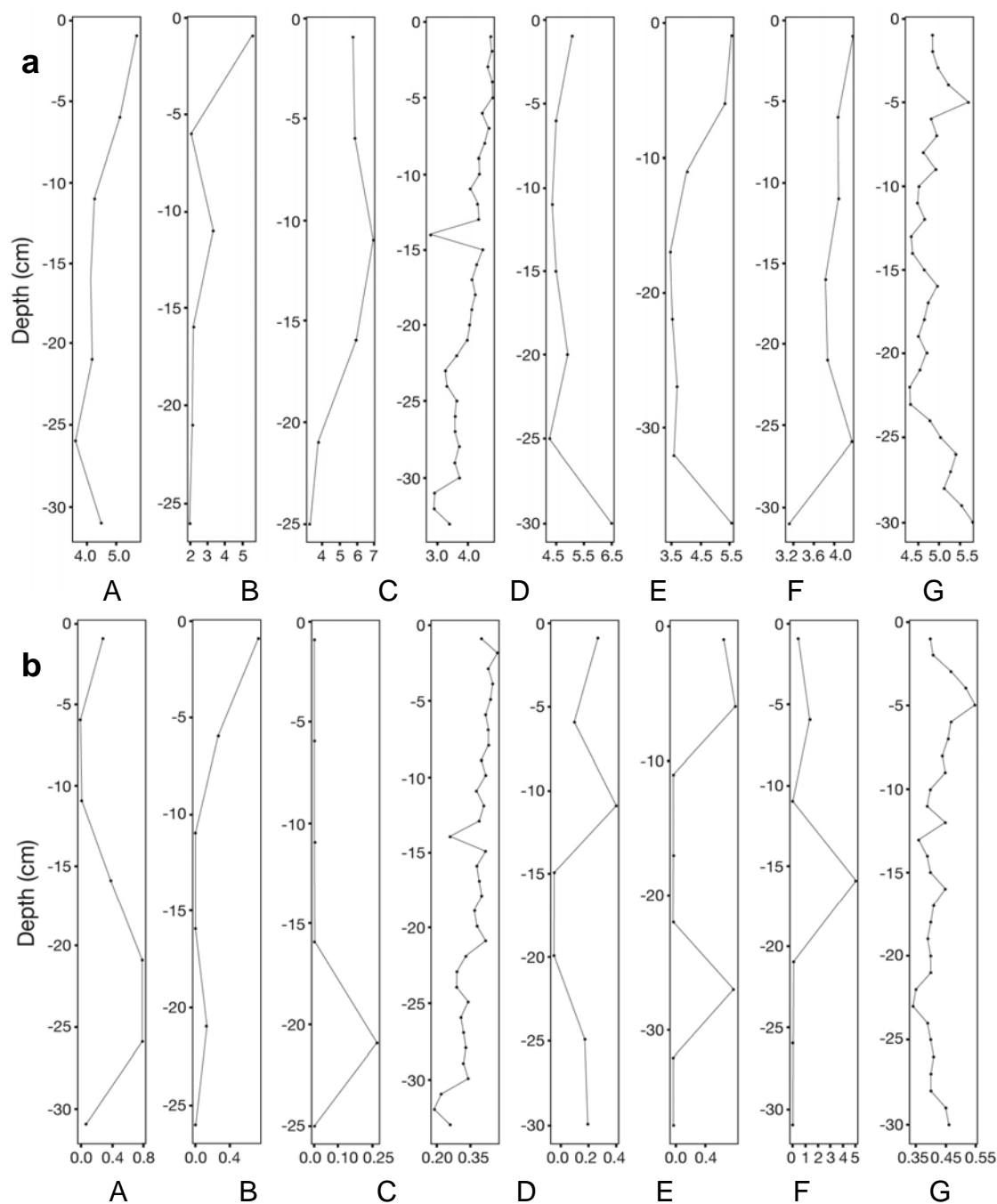
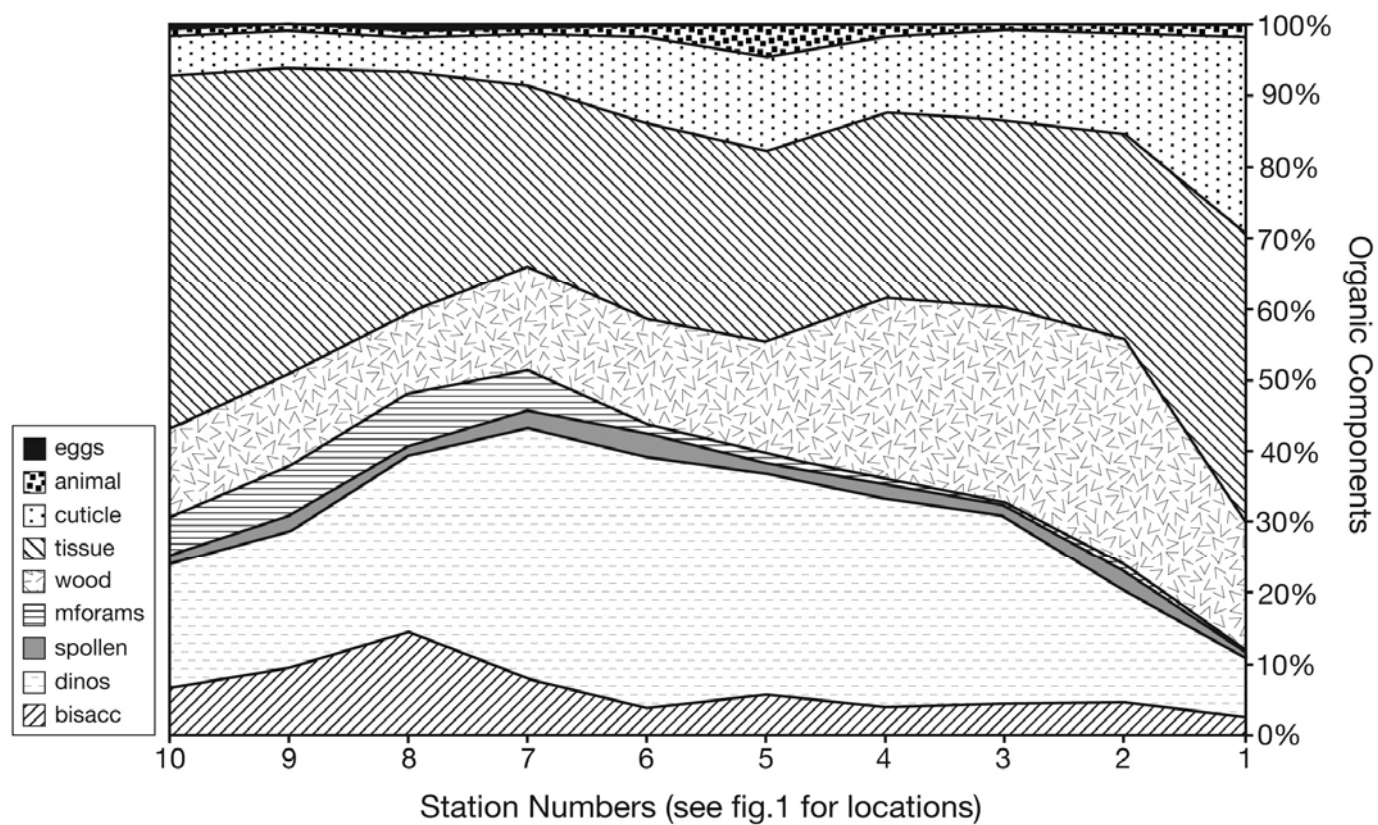


Figure 4. Vertical variation of a) Organic carbon (%) and b) Organic nitrogen (%) in the sampled cores (see Fig.1 for location of samples).

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Figure 5. Variation of organic components from seaward to landward (see Fig.1 for location of samples).

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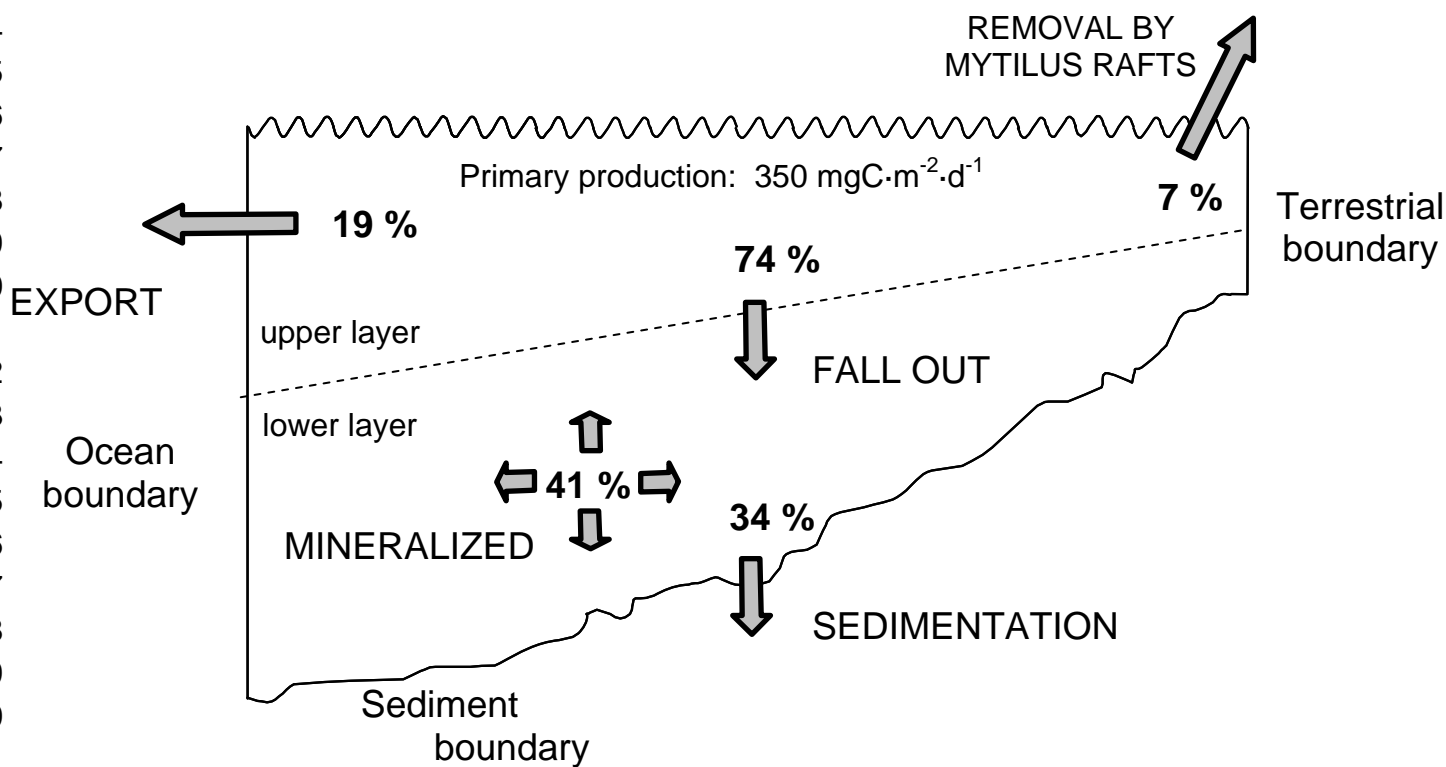


Figure 6. Autochthonous POC production and fluxes in the Ria Vigo

Table 1. Annual ranges and average values of discharges, POC concentrations and loads of the main terrestrial contributors to the Ria of Vigo.

	Fluvial	Oitaven	Alvedosa	Lagares	Fraga	Maior	Ullo
Flow ($\text{m}^3 \cdot \text{s}^{-1}$)	range	1.0 – 173.6	0.11 – 9.58	0.21 – 18.45	0.02 – 2.35	0.02 – 2.35	0.04 – 4.33
	average	16.33	1.63	3.68	0.41	0.40	0.74
[POC] ($\text{mg} \cdot \text{L}^{-1}$)	range	0.08 – 0.74	0.10 – 1.42	0.14 – 5.89	0.16 – 0.57	0.07 – 0.50	0.08 – 1.44
	average	0.18	0.37	1.14	0.33	0.26	0.45
POC Load ($\text{g} \cdot \text{s}^{-1}$)	range	0.1 – 87.7	0.1 – 26.8	0.7 – 3.3	0.3 – 3.0	0.01 – 0.2	0.1 – 0.4
	average	3.52	2.06	1.05	0.87	0.06	0.12
	STP	Arcade	Redondela	Teis	Vigo	Cangas	Moaña
Flow ($\text{m}^3 \cdot \text{s}^{-1}$)	range	0.010 – 0.033	0.058 – 0.087	0.052 – 0.110	1.70 – 2.29	0.040 – 0.099	0.069 – 0.118
	average	0.017	0.073	0.071	1.953	0.061	0.086
[POC] ($\text{mg} \cdot \text{L}^{-1}$)	range	0.12 – 6.55	0.35 – 15.3	0.82 – 68.9	0.39 – 12.6	0.18 – 10.5	0.19 – 6.21
	average	1.62	3.70	29.1	5.07	2.60	1.72
POC Load ($\text{g} \cdot \text{s}^{-1}$)	range	0.01 – 0.07	0.01 – 0.93	0.05 – 4.98	0.74 – 23.4	0.01 – 0.54	0.02 – 0.48
	average	0.03	0.26	2.00	9.71	0.14	0.15

Table 2. POC loads of individual water courses:

$$F = a \cdot Q^2 + b \cdot Q + c$$

POC fluxes, F, are in g s^{-1} with discharges, Q, in $\text{m}^3 \text{s}^{-1}$. R^2 is the correlation coefficient between F and Q.

Type	Source	a	b	c	R^2
Fluvial	Oitaven	0.0024	0.088	0.03	0.999
	Alvedosa	0.350	-0.587	0.28	0.995
	Lagares	0.0019	0.080	0.68	0.749
	Fraga	-0.338	1.95	0.25	0.901
	Maior	-0.0360	0.163	0.01	0.924
	Ullo	-0.0222	0.170	0.03	0.787

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Table 3. Grain counts of organic matter components in the surface sediments of the Ria of Vigo. Number of grains counted was 400.

Component	St.1	2	3	4	5	6	7	8	9	10
bisac	11	19	18	16	23	15	32	58	38	27
dinos	33	62	105	117	125	141	140	99	76	69
spollen	4	11	6	8	6	13	10	5	9	5
mforanms	0	3	2	2	5	5	23	30	28	21
wood	72	128	110	103	63	60	59	45	52	50
tissue	163	115	109	104	107	110	101	136	172	199
cuticle	110	56	51	43	53	48	29	19	21	22
animal	6	6	3	6	17	7	3	4	4	4
eggs	1	0	0	1	2	1	3	4	0	3
lycos	6	7	5	8	7	9	10	16	15	16

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Table 4. Mineral carbon, total organic carbon (TOC), and Rock-eval parameters for selected box-corer samples from San Simón Bay.

Station	Mineral carbon weight %	TOC %	ROCK-EVAL parameters			T max (°C)	mg / g TOC	
			mgHC / g rock S ₁	mg CO ₂ / g rock S ₂	mg CO ₂ / g rock S ₃		iH	iO
B	0.48	5.87	0.06	16.20	9.45	417	275	160
D	0.80	4.43	0.12	13.31	7.45	415	300	168
E	0.89	4.46	0.15	13.40	8.04	415	300	180
F	1.00	4.68	0.22	14.73	8.55	409	314	182
G	1.03	4.28	0.26	12.00	7.75	414	280	181
H	0.95	4.39	0.10	12.05	0.10	414	274	184

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